AIP | The Journal of Chemical Physics

Microwave Spectra, Dipole Moments, Structure, and Ring Puckering Vibration of Cyclobutyl Chloride and Cyclobutyl Fluoride

Hyunyong Kim and William D. Gwinn

Citation: The Journal of Chemical Physics **44**, 865 (1966); doi: 10.1063/1.1726834
View online: http://dx.doi.org/10.1063/1.1726834
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/44/3?ver=pdfcov
Published by the AIP Publishing

we can rewrite (2.15) as follows:

$$G(f,f';E)=(\tfrac{1}{2}\pi)g(f,f';E)+\sum_i\{V_ig(f,i;E)+\alpha_ig_1(f,i;E)\}G(i,f';E)+\sum_i\alpha_ig(f,i;E)G^+(i,f';E). \tag{A2}$$

The equation satisfied by $G^+(i,f';E)$ is given by

$$G^+(i,f';E)=(\tfrac{1}{2}\pi)g_1(i,f';E)+\sum_j\{V_jg_1(i,j;E)+\alpha_jg_2(i,j;E)\}G(j,f';E)+\sum_j\alpha_jg_1(i,j;E)G^+(j,f';E). \tag{A3}$$

The relation between $G(i,f';E)$ and $G^+(i,f';E)$ is

$$(1+\alpha_i)G^+(i,f';E)=(E-V_i)G(i,f';E)-\sum_j\alpha_jJ^{(0)}(i,j)G(j,f';E)-(\tfrac{1}{2}\pi)\delta(i,f'). \tag{A4}$$

Inserting this result into (A2), we get the result

$$\begin{aligned}[1+\sum_i\alpha_i\delta(f,i)]G(f,f';E)=(\tfrac{1}{2}\pi)[g(f,f';E)-\sum_i\{\alpha_i/(1+\alpha_i)\}g(f,i;E)\delta(i,f')]\\ +\sum_i[V_i+\{(1+\alpha_i)^2-1\}E]g(f,i;E)G(i,f';E)(1+\alpha_i)^{-1}\\ -\sum_{i,j}\{\alpha_i\alpha_j/(1+\alpha_i)\}g(f,i;E)J^{(0)}(i,j)G(j,f';E),\end{aligned} \tag{A5}$$

which is equivalent to (3.14) and (3.16), except for the first term in the right-hand side.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 44, NUMBER 3 1 FEBRUARY 1966

Microwave Spectra, Dipole Moments, Structure, and Ring Puckering Vibration of Cyclobutyl Chloride and Cyclobutyl Fluoride*

HYUNYONG KIM† AND WILLIAM D. GWINN
Department of Chemistry, University of California, Berkeley, California

(Received 24 August 1965)

Microwave spectra of nine isotopic species of cyclobutyl chloride and of the normal species of cyclobutyl fluoride have been studied. From the ground state moments of inertia, the structure of cyclobutyl chloride has been determined. Some of the more important structural parameters are: $r(C_\alpha–C_\beta)=1.525\pm0.005$ Å $r(C_\beta–C_\gamma)=1.550\pm0.005$ Å, $r(C_\alpha–Cl)=1.775\pm0.005$ Å, $\angle Cl–(C_\beta C_\alpha C_\beta)=135°\pm1°$, and $\angle(C_\beta C_\alpha C_\beta)–(C_\beta C_\gamma C_\beta)=20°\pm1°$. The chlorine atom is found at the equatorial position of the puckered ring, and the axial form was not observed. Quadrupole coupling constants of the chlorine atom for $CH_2CH_2CH_2CH^{35}Cl$ species were found to be $\chi_{aa}=-56.58\pm0.10$ Mc/sec and $\chi_{cc}=23.60\pm0.1$ Mc/sec. The transformed coupling constant along the C–Cl bond is -65.98 Mc/sec (assuming the quadrupole tensor was axially symmetric about the C–Cl bond). The moments of inertia of cyclobutyl fluoride calculated using $r(C–F)=1.37$ Å, $\angle F–(C_\beta C_\alpha C_\beta)=132°$ and the remaining structural parameters of cyclobutyl chloride agreed with the observed moments of inertia. The dipole moments of cyclobutyl fluoride were determined by the Stark effect: $\mu_a=1.870\pm0.005$ D, $\mu_c=0.52\pm0.02$ D, and $\mu=1.94\pm0.01$ D.

INTRODUCTION

PREVIOUS work on the ring puckering of four-membered rings has indicated that cyclobutane has a moderately high barrier at the planar configuration. This was observed in the infrared and Raman spectrum.[1] At low temperatures the spectra were best interpreted by using the selection rules corresponding to D_{2d} symmetry (puckered ring). As the temperature was increased and higher puckering vibrational states became more populated, absorption lines corresponding to the planar configuration appeared in increasing intensity. From these measurements a rough estimate of the barrier to the planar configuration was given as 400 cm^{-1}. Electron diffraction studies[2] at room temperature gave an indication that the ring is probably puckered and that the angle of ring puckering is about 20°. More recent infrared and Raman spectra[3] have

---

* From the doctoral thesis of Hyunyong Kim, University of California, 1964. This work has been presented at the American Physical Society meeting in Washington, D.C. in 1965: see Bull. Am. Phys. Soc. Ser. 11, **10**, 491 (1965).

† Present address: Department of Chemistry, Miami University, Oxford, Ohio.

[1] W. D. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, J. Am. Chem. Soc. **75**, 5634 (1953).

[2] J. D. Dunitz and V. Schomaker, J. Chem. Phys. **20**, 1703 (1952).

[3] R. C. Lord and I. Nakagawa, J. Chem. Phys. **39**, 2951 (1963).

also been best interpreted on the basis of a puckered ring for cyclobutane.

A related molecule, trimethylene oxide, has been studied extensively using microwave spectroscopy[4] and far-infrared spectroscopy.[5,6] For this molecule the complete potential function has been determined and it was found that the molecule is essentially planar but the potential function does have a double minimum with a 17-cm^{-1} barrier to the planar configuration which lies 6 cm^{-1} below the zero-point vibration.

It would be most interesting to obtain a more definite barrier for cyclobutane using the techniques of microwave spectroscopy. This is impossible, since cyclobutane has no dipole moment. The halogen derivatives do have dipole moments and this study of monohalogenated cyclobutane was undertaken. The monohalogen derivatives also have the possibility of existing in two possible configurations if the barrier to puckering is high compared to the lower ring puckering vibrational levels. The halogen atom can be situated at either the axial or equatorial position of the puckered cyclobutane ring, and this would make the ring puckering potential asymmetric with respect to the planar ring configuration.

An introduction of a halogen atom to the cyclobutane ring reduces the molecular symmetry to only one element C_s. The only low-frequency vibration which would be expected, other than ring puckering, is the carbon halogen bending.

We have studied the microwave spectra of nine isotopic species of cyclobutyl chloride and normal cyclobutyl fluoride. From the observed spectra, the structure and the nuclear quadrupole constants of cyclobutyl chloride and the dipole moment of cyclobutyl fluoride have been determined. The energy-levels of the ring puckering vibration were found from the measurement of the relative intensities of the vibrational satellites. The microwave spectrum of cyclobutyl bromide has been published.[7] They report that cyclobutyl bromide is permanently puckered at the ground state with the dihedral angle of 29°22′±08′.

EXPERIMENTAL

Cyclobutyl chloride was first prepared by Perkin in 1894 from the reaction of cyclobutanol (prepared from cyclobutylamine hydrochloride and silver nitrite) with phosphorous pentachloride,[8] and more recently by Roberts and Mazur from the vapor-phase photochlorination of cyclobutane.[9] In this work, the normal cyclobutyl chloride was prepared by the method of Roberts and Mazur and the deuterated species by Perkin's method.[10] The α-monodeutero-cyclobutanol was obtained by the reaction of cyclobutanone with $LiAlD_4$. To obtain the α-monodeutero-β-tetradeutero-cyclobutanol, the β hydrogens of cyclobutanone were deuterated in the slightly acidic medium of D_2O with D_2SO_4 as catalyst, and then treated with $LiAlD_4$. During the reaction of cyclobutanol with PCl_5, an extensive rearrangement among the β- and γ-methylene groups was observed.[10] The product consisted of $CH_2CD_2CD_2CDCl$[10a] and $CD_2CH_2CD_2CDCl$ with the composition ratio of 2:1.

Cyclobutyl fluoride has never been reported. It was prepared by replacing the chlorine atom in cyclobutyl chloride with the fluorine atom using a powdered mixture of AgF and CaF_2. The progress of the replacement reaction was followed by observing the change in intensity of the microwave absorption by cyclobutyl chloride. The replacement reaction was rapid, and the gas chromatographic analysis of the product showed only one peak. The identification of cyclobutyl fluoride was made through the assignment of its rotational spectrum.

The spectrograph used in this work was a 5-kc/sec Stark modulated spectrometer with the absorption cell cooled at −70°C. The frequency measurements were made with a phase-stabilized klystron lock-in system.[11] The frequency range of 8 to 35 Gc/sec was covered.

MICROWAVE SPECTRA

The rotational constants of cyclobutyl chloride calculated from a trial structure predicted a slightly asymmetric prolate top ($\kappa \cong 0.9$) and transitions due to both a and c components of the dipole moment. A series of R-branch transitions were observed and assigned by their characteristic Stark effects and the hyperfine structures arising from the interaction of the over-all rotation of the molecule with the electric quadrupole moment of the chlorine nucleus. The weak Q-branch transitions for the a component of the dipole moment were identified for the species

$$CH_2CH_2CH_2CH^{35}Cl$$

only, while the corresponding c-type transitions were not observed. For the $CH_2CH_2CH_2CH^{35}Cl$ species, the rotational constants B and C were calculated from the 1_{10}–2_{11} and the 1_{11}–2_{12} transitions which occur at frequencies of $(3B+C)$ and $(B+3C)$, respectively. The constant A was calculated from the observed Q-branch transitions. The frequencies calculated with the rota-

---

[4] S. I. Chan, J. Zinn, J. Fernandez, and W. D. Gwinn, J. Chem. Phys. **33**, 1643 (1960); **34**, 1319 (1961).

[5] A. Danti, W. J. Lafferty, and R. C. Lord, J. Chem. Phys. **33**, 294 (1960).

[6] T. Borger, J. Russell, H. Strauss, S. I. Chan, and W. D. Gwinn (to be published). The energies quoted above correspond to this paper.

[7] W. G. Rothschild and B. P. Dailey, J. Chem. Phys. **36**, 2931 (1962).

[8] W. H. Perkin, Jr., J. Chem. Soc. **65**, 950 (1894).

[9] J. D. Roberts and R. H. Mazur, J. Am. Chem. Soc. **73**, 2515 (1951).

[10] H. Kim and W. D. Gwinn, Tetrahedron Letters **37**, 2535 (1964).

[10a] *Note added in proof*: Throughout this paper, it is assumed in writing the formulas for cyclobutane derivatives and their isotopic species that the first and last carbons are the ones connected to form the four-membered rings.

[11] A. Narath and W. D. Gwinn, Rev. Sci. Instr. **33**, 79 (1962).

tional constants are compared with these observed frequencies in Table I. It is seen that the centrifugal distortion effects are fairly small for the transitions which were studied.

The spectra of other isotopic species studied followed the rigid asymmetric rotor energy pattern with $\kappa \cong -0.9$. The rotational constants for these species were calculated by fitting the R-branch transitions of the lowest J value to a rigid-rotor formula. For these species, the rotational constant A contains rather large uncertainty of 5 Mc/sec, because the a-type R-branch transitions of the near prolate rotor are insensitive to the value of A. The weak spectrum of $^{13}CH_2CH_2CH_2CH^{35}Cl$ species was observed in its natural abundance. It was distinguished from the vibrational satellites by observing the temperature dependence of the intensities. The observed transitions of these isotopic species are listed in Table II. Since all the observed transitions showed the hyperfine splittings due to the interaction of over-all rotation of the molecule with the quadrupole moments of the chlorine nucleus, the frequencies given in Tables I and II are the hypothetical unsplit frequencies. The treatment of this interaction is found in the standard texts.[12] The resolved hyperfine components of four isotopic species are given in Table III. The ground-state rotational constants of all the species studied are listed in Table IV. Besides the ground-state spectrum, satellite lines have been observed for all the species studied except the $^{13}CH_2CH_2CH_2CH^{35}Cl$ species.

TABLE I. Assigned ground-state transitions of $CH_2CH_2CH_2CH^{35}Cl$ (I).

Transitions	Measured[a] in Mc/sec	Calculated in Mc/sec
1_{11}–2_{12}	9 110.03	9 109.98
1_{10}–2_{11}	9 758.93	9 758.90
1_{01}–2_{02}	9 424.29	9 424.24
2_{02}–3_{03}	14 110.80	14 110.86
2_{12}–3_{13}	13 658.81	13 658.68
2_{11}–3_{12}	14 631.90	14 631.86
3_{03}–4_{04}	18 767.32	18 767.33
3_{13}–4_{14}	18 199.84	18 200.12
3_{12}–4_{13}	19 496.75	19 496.75
3_{22}–4_{23}	18 860.86	18 860.93
4_{04}–5_{05}	23 384.78	23 384.78
4_{14}–5_{15}	22 731.91	22 732.32
4_{13}–5_{14}	24 350.04	24 350.40
7_{17}–7_{16}	9 044.8±0.1	9 044.9
8_{18}–8_{17}	11 591.1±0.1	11 591.2
9_{19}–9_{18}	14 421.1±0.1	14 421.2
$10_{1,10}$–10_{19}	17 512.8±0.1	17 512.9

[a] The experimental error in frequency measurement is ±0.03 Mc/sec unless otherwise indicated.

The approximate rotational constants of cyclobutyl fluoride were calculated using the structural parameters of cyclobutyl chloride (see the following section on structure) and the C–F bond distance of 1.37 Å. A search was made for the transitions that arise from

TABLE II. Assigned ground-state transitions of various isotopic species of cyclobutyl chloride.[a]

Transitions	II[b]	III	IV	V	VI	VII	VIII	IX
1_{11}–2_{12}	8 893.39	9 078.59	9 135.31					
1_{10}–2_{11}	9 510.61	9 667.23						
1_{01}–2_{02}	9 192.72	9 364.04	9 423.31					
2_{02}–3_{03}	13 766.30	14 023.69	13 682.93			12 809.57	12 498.3	
2_{12}–3_{13}	13 334.40	13 612.53	13 290.01			12 436.62		
2_{11}–3_{12}	14 259.99	14 495.10	14 129.80			13 242.01	12 908.1	
3_{03}–4_{04}	18 312.60	18 657.06	18 206.86	17 741.1	17 318.9	17 038.62	16 627.6	
3_{13}–4_{14}	17 768.90	18 139.59	17 710.95	17 175.1	16 773.0	16 572.12	16 180.0	
3_{12}–4_{13}	19 002.02	19 316.17	18 830.10	18 583.5		17 645.25		
3_{22}–4_{23}	18 396.64	18 738.88	18 280.42			17 119.59		
4_{04}–5_{05}	22 823.75	23 256.64	22 700.00	22 053.6		21 234.06	20 726.9	23 210.6
4_{14}–5_{15}	22 194.80	22 659.10	22 124.21	21 439.4	20 939.6	20 699.73	20 211.6	22 550.0
4_{13}–5_{14}	23 734.73	24 127.02	23 521.42	23 192.6	22 608.5	22 038.68	21 485.4	24 208.2
5_{05}–6_{06}				26 298.7	25 694.4		24 790.3	27 739.5
5_{15}–6_{16}				25 686.9	25 090.8		24 234.0	27 033.0
5_{14}–6_{15}				27 773.7	27 079.6		25 758.3	29 016.2
6_{06}–7_{07}				30 481.6	29 792.1			32 217.0
6_{16}–7_{17}				29 916.5	29 225.8			31 503.2
6_{15}–7_{16}				32 318.9	31 518.6			33 802.5

[a] Frequencies are in megacycles per second and are accurate to ±0.03 Mc/sec for Isotopes II, III, IV, and VII and to ±0.1 Mc/sec for Isotopes V, VI, VIII, and IX.

[b] Reference to the isotopic species is given in Table IV.

---

[12] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), and M. W. P. Strandberg, *Microwave Spectroscopy* (Methueu and Company, Ltd., London, 1960), and W. Gordy, W. V. Smith, and R. F. Trambarulo, *Microwave Spectroscopy* (John Wiley & Sons, Inc., NewYork, 1953).

TABLE III. Observed frequencies of hyperfine components.[a]

Transitions	F–F′	Obs. (Mc/sec)	$\Delta\nu$[b]	Obs. (Mc/sec)	$\Delta\nu$
		$CH_2CH_2CH_2CH^{35}Cl$		$CH_2CH_2CH_2CD^{35}Cl$	
1_{11}–2_{12}	3/2–5/2	9 099.25	0.03	9 067.70	−0.02
	3/2–3/2	9 103.45	0.02	9 071.95	−0.02
	5/2–5/2	9 107.45	−0.01	9 075.95	0.0
	5/2–7/2	9 113.34	−0.03	9 081.90	0.0
	1/2–3/2	9 118.33	0.05	9 086.80	0.02
	1/2–1/2	9 124.23	0.05	···	···
1_{10}–2_{11}	3/2–5/2	9 748.32	0.0	9 656.61	0.02
	3/2–3/2 }	9 754.21	0.0	9 662.48	0.01
	5/2–5/2 }		−0.01	9 662.65	−0.04
	5/2–7/2	9 762.47	0.0	9 670.77	0.0
	1/2–3/2	9 764.85	0.02	9 673.17	−0.01
	1/2–1/2	9 773.15	0.07	9 681.37	−0.04
1_{01}–2_{02}	1/2–3/2	9 410.15	0.01	9 349.90	0.04
	5/2–5/2	9 411.41	0.01	9 351.10	−0.02
	1/2–1/2	9 424.25	0.03	9 364.00	0.02
	5/2–7/2	9 425.47	−0.01	9 365.22	0.0
	3/2–5/2	···	···	···	···
	3/2–3/2	9 425.61	0.0	9 375.38	0.0
		$CH_2CH_2CH_2CH^{37}Cl$		$CH_2CH_2CH_2CD^{37}Cl$	
3_{22}–4_{23}	3/2–5/2	18 399.80	−0.01	18 283.59	0.04
	9/2–11/2	18 398.26	0.01	18 282.02	−0.01
	5/2–7/2	18 395.38	0.01	18 279.13	0.0
	7/2–9/2	18 393.58	−0.03	18 277.58	0.03

[a] Frequencies are in megacycles per second and good to ±0.02 Mc/sec.

[b] Deviation from the calculated frequency (obs. freq.−calc. freq.). The coupling constants used for the calculated frequencies are determined later in the paper and are listed in Table X.

TABLE IV. Rotational constants of the ground state of cyclobutyl chloride.[a]

Isotopic species	A	B	C
$CH_2CH_2CH_2CH^{35}Cl$(I)	10 086.7±0.5	2520.84	2196.38
$CH_2CH_2CH_2CH^{37}Cl$(II)	10 085	2454.78	2146.17
$CH_2CH_2CH_2CD^{35}Cl$(III)	9 620	2490.39	2196.07
$CH_2CH_2CH_2CD^{37}Cl$(IV)	9 620	2425.81	2145.84
$CD_2CH_2CD_2CD^{35}Cl$(V)	7 540	2415.75	2062.87
$CD_2CH_2CD_2CD^{37}Cl$(VI)	7 539	2352.20	2016.44
$CH_2CD_2CD_2CD^{35}Cl$(VII)	8 263	2275.08	2006.51
$CH_2CD_2CD_2CD^{37}Cl$(VIII)	8 257	2216.02	1960.62
$C^{13}H_2CH_2CH_2CH^{35}Cl$(IX)	9 860	2509.03	2176.44

[a] The constants are in megacycles per second and the uncertainties in B and C are ±0.03 Mc/sec and that in A is ±5 Mc/sec unless specified otherwise.

both *a*- and *c*-type transitions. The observed spectrum was very similar to the spectrum of cyclobutyl chloride. A rigid-rotor assignment was made for both *a*- and *c*-type transitions. The assigned transitions are listed in Table V. The trial rotational constants calculated using the structural parameter of cyclobutyl chloride were found to be within 0.3% of the experimentally obtained values. For the sum, $2\sum m_ib_i^2=(I_a+I_c-I_b)$ to which the halogen atom makes no contribution, the observed value of 79.63 amu·Å^2 may be compared to that of 79.74 amu·Å^2 which was found in cyclobutyl chloride. The good agreement obtained between the observed and the calculated moments of inertia and also the low-frequency vibrational states observed were taken to be sufficient evidence for the identification of cyclobutyl fluoride.

TABLE V. Assigned transitions of cyclobutyl fluoride.[a]

Transition	Ground state	1st excited	2nd excited	3rd excited
1_{01}–2_{02}	15 266.36	15 295.41	15 333.42	15 385.11
1_{11}–2_{12}	14 482.76	14 512.22	14 550.90	14 603.34
1_{10}–2_{11}	16 227.34	16 258.50	16 298.92	16 353.10
2_{02}–3_{03}	22 683.68	22 724.29	22 777.71	22 851.36
2_{12}–3_{13}	21 671.24	21 714.65	21 771.78	
2_{11}–3_{12}	24 282.12	24 328.20	24 387.84	24 468.12
2_{21}–3_{22}	23 032.56	23 078.00	23 137.32	23 217.24
3_{03}–4_{04}	29 873.23	29 922.72	29 989.12	30 081.32
3_{13}–4_{14}	28 803.88	28 860.52	28 935.27	29 037.39
3_{12}–4_{13}	32 259.12	32 318.26	32 395.50	32 499.60
4_{14}–4_{13}	8 683.52			
5_{15}–5_{14}	12 928.32			
0_{00}–1_{10}	14 525.30			
1_{01}–2_{11}	23 075.16			
1_{11}–2_{21}	35 026.04			

[a] Frequencies are in megacycles per second and accurate to ±0.02 Mc/sec.

GROUND STATE-STRUCTURE

Assuming that the β-methylene and the γ-methylene hydrogen angles are bisected by the respective planes of the ring[13] and that the molecule possesses a plane of symmetry through the α- and γ-carbon atoms, there are 14 structural parameters in cyclobutyl chloride. These are six bond distances and eight bond angles. There is sufficient data to determine the substitution coordinates[14] of the H_α, C_β, and Cl atoms. Since the H_α and Cl atoms are located on the plane of symmetry, two of these nine coordinates have already been assumed, and seven of the 14 structural variables remained to be determined. They were determined

---

[13] Calculations were also made without this assumption. The angles in this assumption were found to be equal. The increase in the number of variables decreased the definitiveness of other variables and it was felt that it was best to make this assumption.

[14] J. Kraitchman, Am. J. Phys. 21, 17 (1953).

by expanding the 22 independent moments of inertia in a Taylor series,[15]

$$I_k{}^j(\text{obs.})=I_k{}^j(\text{calc.})+\sum_i(\partial I_k{}^j/\partial x_i)\Delta x_i,$$

where $I_k{}^j$ is the kth principal moment of inertia for the isotopic species j, and x_i is a structural parameter. With these relations a set of structural parameters is sought such that the moments of inertia calculated using this set are equal to the observed moments of inertia. The coefficients, $(\partial I_k{}^j/\partial x_i)$, are determined by assuming a trial structure and then calculating the change in $I_k{}^j$ for a given change in x_i, with all other x_i's held constant. The new Δx_i's calculated to reproduce the observed moments of inertia are then applied as a correction to the previously assumed structure. This process was repeated by an IBM 7090 computer until a satisfactory agreement was reached. The coordinates thus obtained are listed in Table VI. The moments of inertia calculated using this set of coordinates and the observed moments of inertia are listed in Table VII.

TABLE VI. Coordinates for cyclobutyl chloride (in angstroms).

Atoms	*a*	*b*	*c*
Chlorine	1.661	0.00	0.092
α-carbon	0.028	0.00	−0.454
α-hydrogen	−0.16	0.00	−1.548
β-carbon	−0.980	1.086	0.033
β_1-hydrogen	−0.667	1.527	0.973
β_2-hydrogen	−1.172	1.839	−0.725
γ-carbon	−2.077	0.00	0.169
γ_1-hydrogen	−2.592	0.00	1.141
γ_2-hydrogen	−2.814	0.00	−0.648

It is rather difficult to state the range of uncertainties associated with the coordinates thus determined. In cyclobutyl chloride, there is a low-frequency ring puckering vibration (to be discussed in the following section), and the principal atoms such as carbon and chlorine are located quite close to either one of the principal axes. The approximate uncertainties cited for the structure in Table VIII are considerably greater than those involved in fitting the observed moments of

TABLE VII. Effective moments of inertia (amu·Å²) of cyclobutyl chloride[a] in the lowest vibrational level.

Isotopic species		I*a*	I*b*	I*c*	I*a*+I*c*−I*b*
$CH_2CH_2CH_2CH^{35}Cl$(I)	obs.	50.119	200.541	230.166	79.944
	calc.	50.09	200.01	229.7	
$CH_2CH_2CH_2CH^{37}Cl$(II)	obs.	50.13	205.937	235.550	79.74
	calc.	50.11	205.5	235.2	
$CH_2CH_2CH_2CD^{35}Cl$(III)	obs.	52.55	202.993	230.198	79.75
	calc.	52.48	202.5	229.7	
$CH_2CH_2CH_2CD^{37}Cl$(IV)	obs.	52.55	208.397	235.587	79.74
	calc.	52.49	207.9	235.1	
$CD_2CH_2CD_2CD^{35}Cl$(V)	obs.	67.05	209.265	245.062	102.85
	calc.	66.95	209.0	244.7	
$CD_2CH_2CD_2CD^{37}Cl$(VI)	obs.	67.07	214.918	250.705	102.85
	calc.	66.96	214.7	250.4	
$CH_2CD_2CD_2CD^{35}Cl$(VII)	obs.	61.19	222.204	251.945	90.93
	calc.	61.28	221.8	251.3	
$CH_2CD_2CD_2CD^{37}Cl$(VIII)	obs.	61.21	228.126	257.842	90.93
	calc.	61.29	227.7	257.4	
$CH_2CH_2CH_2CH^{35}Cl$(IX)	obs.	51.27	201.485	232.274	82.06
	calc.	51.25	201.1	231.8	

[a] Conversion factor used: I*a*(in amu·Å²)$=5.05531\times10^5/A$ (in megacycles per second). Errors in I*b* and I*c* are ±0.003 and that in I*a* is ±0.03.

---

[15] T. E. Turner and J. A. Howe, J. Chem. P.hys **24**, 924 (1956).

TABLE VIII. Ground-state structure of cyclobutyl chloride.

$r(C_\alpha\text{–}Cl)=1.775\text{Å}$	±0.005	$HC_\alpha Cl=114^\circ\pm2^\circ$
$r(C_\alpha\text{–}C_\beta)=1.525$	±0.005	$Cl\text{–}(C_\beta C_\alpha C_\beta)=135^\circ\pm1_\circ$
$r(C_\beta\text{–}C_\gamma)=1.550$	±0.005	$(C_\beta C_\alpha C_\beta)\text{–}(C_\beta C_\gamma C_\beta)=20^\circ\pm1^\circ$
$r(C_\alpha\text{–}H)=1.10$	±0.01	$C_\beta C_\alpha C_\beta=90^\circ50'\pm30'$
$r(C_\beta\text{–}H)=1.085$	±0.01	$HC_\beta H=112^\circ\pm1^\circ$
$r(C_\gamma\text{–}H)=1.10$	±0.01	$HC_\gamma H=110^\circ\pm1^\circ$
		$H_1C_\beta C_\alpha=114^\circ\pm1^\circ$
		$H_2C_\beta C_\alpha=115^\circ\pm1^\circ$

inertia. They are estimated so as to encompass the effects of the vibration–rotation interaction. The interesting features of the structure are: the four-membered carbon ring is bent with a dihedral angle, $\angle(C_\beta C_\alpha C_\beta)$–$(C_\beta C_\gamma C_\beta)$ of 20°, and the chlorine atom is located at the equatorial position, and the C_α–C_β bond distance of 1.525 Å is shorter than the C_β–C_γ bond distance of 1.550 Å.

In cyclobutyl fluoride, only one isotopic species was studied and the structure determination is not possible. If the C–F distance is taken as 1.37 Å and all other structural parameters are taken to be the same as in cyclobutyl chloride, there is good agreement between the moments of inertia so calculated and those observed experimentally. Of particular interest is $\sum m_i b_i^2=\frac{1}{2}(I_a+I_c-I_b)$ which does not depend upon the position of the halogen. In cyclobutyl fluoride it is 79.634 amu·Å^2 and in cyclobutyl chloride it is 79.744 amu·Å^2. A slightly better agreement is obtained when the angle between the C–F bond and the $C_\beta C_\alpha C_\beta$ plane is taken to be 132° instead of 135° as was found in cyclobutyl chloride. The calculated moments of inertia using these parameters are included in Table IX.

QUADRUPOLE COUPLING CONSTANTS OF CYCLOBUTYL CHLORIDE

From the results of the hyperfine structure analysis, the quantities χ_{aa} and χ_{cc}, where $\chi_{aa}=eQ(\partial^2V/\partial a^2)$, etc. were obtained. They are the diagonal elements of the quadrupole coupling tensor in the principal inertial axis system. χ_{bb} can be obtained from the relation $\chi_{aa}+\chi_{bb}+\chi_{cc}=0$. The off-diagonal elements χ_{ab} and χ_{bc} are zero by the symmetry of the molecule, but χ_{ac} is not necessarily zero. These off-diagonal elements of the quadrupole coupling tensor in the asymmetric-top molecule are usually determined either from the second-order quadrupole energy perturbation, or from the observed quadrupole coupling constants of two isotopic species, with the assumption that the electrostatic potential in the neighborhood of the chlorine nucleus is the same in both species. In the case of cyclobutyl chloride, neither of these methods proved to be applicable. The calculation of the rotational energy levels showed no near-degenerate levels of correct symmetries to give the observable second-order effect. Though the quadrupole constants of several different isotopic species have been determined in this work, the changes introduced by the isotopic substitutions were too small, after correction for Q^{35}/Q^{37}, to permit a determination of the axis of the quadrupole tensor.

In order to relate the diagonal elements of the quadrupole tensor to the actual bond properties, it is assumed that one of the principal axes of the quadrupole tensor coincides with the C–Cl bond; that is, the C–Cl bond is not bent. The axis system x, y, z, is defined such that the z axis coincides with the C–Cl bond and the y axis is perpendicular to the symmetry plane of the molecule. With the angle ρ between the a and z axes obtained from the structure, χ_{aa} and χ_{cc} were

TABLE IX. Rotational constants and the moments of inertia of cyclobutyl fluoride.[a]

	Ground state	1st excited state	2nd excited state	3rd excited state
A	10 250.42	10 176±2	10 094±2	10 002±2
B	4 274.91	4 282.91	4 293.23	4 306.99
C	3 402.62	3 409.77	3 419.22	3 432.12
Ia	49.318	49.679	50.082	50.543
Ia (calc)[b]	(49.35)			
Ib	118.255	118.034	117.751	117.375
Ib (calc)[b]	(118.24)			
Ic	148.571	148.260	147.850	147.295
Ic (calc)[b]	(148.62)			
Ia+Ic−Ib	79.634	79.905	80.181	80.463
Vibrational energy level		equally spaced by 140±20 cm^{-1}		

[a] Rotational constants are in megacycles per second and the moments of inertia are in amu·Å^2. Uncertainties in the rotational constants are ±0.02 Mc/sec unless otherwise indicated. The conversion factor used is I_a(amu·Å^2) = $5.05531\times10^5/A$ (in megacycles per second).

[b] The values in parentheses are calculated using the structural parameters of cyclobutyl chloride with the C–F bond distance of 1.37 Å and the angle between the C–F bond and the $C_\beta C_\alpha C_\beta$ plane equal to 132°.

TABLE X. Quadrupole coupling constants (in megacycles per second) of cyclobutyl chloride.

Isotopic species	χ_{zz} obs.	χ_{zz} calc.[a]	χ_{xx} obs.	χ_{xx} calc.	ρ[b]
$CH_2CH_2CH_2CH^{35}Cl$	−56.58±0.10	−56.62	23.60±0.10	23.64	17°55′
$CH_2CH_2CH_2CH^{37}Cl$	−44.67	−44.93	18.58	18.84	17°45′
$CH_2CH_2CH_2CD^{35}Cl$	−56.72	−56.68	23.80	23.76	17°51′
$CH_2CH_2CH_2CD^{37}Cl$	−44.66	−44.96	18.74	18.99	17°43′

[a] Calculated with $\chi_{zz}=-65.98$, $\chi_{xx}=32.98$, and $Q^{35}/Q^{37}=1.2628$. [b] Angle between the C–Cl bond and the *a* axis calculated from the coordinates in Table VI.

calculated with the two parameters χ_{zz} and χ_{xx}. The best fit from this calculation is obtained with bond constants (for ^{35}Cl): $\chi_{zz}=-65.98$ Mc/sec and $\chi_{xx}=32.98$ Mc/sec. $\chi_{bb}=\chi_{yy}=32.98$ Mc/sec is independent of the angle ρ. The observed and calculated coupling constants are listed in Table X. The experimental uncertainty in the angle ρ is about 30′ and this leads to an uncertainty of 1% in χ_{zz}.

DIPOLE MOMENT OF CYCLOBUTYL FLUORIDE

The dipole moment of cyclobutyl fluoride in the ground state has been determined by the Stark effect. The spacing of the Stark electrode in the waveguide was calibrated with the $J=1\rightarrow 2$ transitions of OCS.[16] The Stark coefficients for the $M=0$ components of $1_{11}-2_{12}$ and $1_{10}-2_{11}$ and both $M=0$ and $M=1$ components of $1_{01}-2_{02}$ transitions were calculated by second-order perturbation theory.[17] The calculated coefficients and the observed values of $\Delta\nu/E^2$ are listed in Table XI. From these data, $\mu_a=1.870\pm0.005$ D, $\mu_c=0.52\pm0.02$ D, and $\mu=1.94\pm0.01$ D were obtained. For the $M=1$ components of $1_{11}-2_{12}$ and $1_{10}-2_{11}$ transitions, nonquadratic Stark effect was observed due to the strong perturbation of the near-degenerate 1_{11} and 1_{10} levels. The Hamiltonian matrix for the rotational energy and Stark perturbation was reduced to the 2×2 block and then diagonalized. The calculated Stark displacements using the value of the dipole moment determined above and the observed displacements agreed within the experimental uncertainty, and this provided an independent determination of the dipole moment. The total dipole makes an angle of 15°32′ with the *a* axis. The dipole moments of the first and the second excited states have been measured. The measured values fall within the experimental uncertainties of the ground-state value.

VIBRATIONAL SATELLITES

Cyclobutyl chloride, as in the case of cyclobutane, is expected to have a low-frequency ring puckering vibration below 200 cm^{-1} and in addition, the carbon-chlorine deformation[18] around 300–400 cm^{-1}. We would then expect some of these excited states of low-frequency vibrations to be appreciably populated at room temperature, and consequently to give rise to satellite lines in the rotational spectrum. Three of these vibrational satellites besides the ground state have been observed in the cyclobutyl chloride spectrum. The rotational transitions and the rotational constants of the excited states are given in Table XII. They are listed in order of decreasing intensity. The microwave intensity measurements for several rotational transitions were made at the two temperatures, 298° and 208°K. Upon averaging all the measurements, the vibrational energy levels were found to be 155, 300, and 380 cm^{-1} above the ground state with an uncertainty of 15 cm^{-1}. The infrared spectrum of gaseous cyclobutyl chloride was obtained with a Beckman IR-12. The pressure was 75 mm Hg. In the spectrum range of 250 to 500 cm^{-1}, a strong absorption with a sharp *Q*-branch band at 371 cm^{-1} and a weak absorp-

TABLE XI. Stark coefficients and the observed values of $\Delta\nu/E^2$ of cyclobutyl fluoride.[a]

Transitions	M	$C\times10^5$ (Mc/sec)$^{-1}$	$D\times10^5$ (Mc/sec)$^{-1}$	$\Delta\nu/E^2\times10^5$ (Mc/sec/V^2)
$1_{01}-2_{02}$	0	−1.9854	0.9871	−9.22±0.03
	1	1.6091	3.1437	9.00±0.03
$1_{11}-2_{12}$	0	1.7080	0.2432	8.31±0.02
$1_{10}-2_{11}$	0	1.5244	−0.9731	7.03±0.02

[a] C and D in the equation, $\Delta\nu/E^2=C\mu_a^2+D\mu_c^2$.

---

[16] S. A. Marshall and J. Weber, Phys. Rev. **105**, 1502 (1957).

[17] S. Golden and E. B. Wilson, Jr., J. Chem. Phys. **16**, 669 (1948).

[18] N. T. McDevitt, A. L. Rozek, F. F. Bentley, and A. D. Davidson, J. Chem. Phys. **42**, 1173 (1965).

TABLE XII. Assigned transitions and rotational constants (in megacycles per second) of the excited states of cyclobutyl chloride.

Transitions	$\nu_\alpha=1$	$\nu_\alpha=2$	$\nu_\beta=1$
	$\overline{\mathrm{CH_2CH_2CH_2CH}}{}^{35}\mathrm{Cl}$		
2_{02}–3_{03}	14 141.20±0.1	14 179.6±0.1	
2_{12}–3_{13}	13 690.15	13 729.1	
2_{11}–3_{12}	14 661.90	14 699.8	
5_{05}–6_{06}	28 028.3	28 088.1	28 204.5±0.1
5_{15}–6_{16}	27 317.3	27 392.2	27 511.0
5_{14}–6_{15}	29 252.6	29 323.2	29 429.2
6_{06}–7_{07}	32 546.9	32 630.6	32 768.4
6_{16}–7_{17}	31 833.6	31 924.2	32 063.1
6_{15}–7_{16}	34 078.9	34 164.8	34 289.2
$A-A_0$	−57	−178	−146
$B-B_0$	+5.06	+11.20	+19.30
$C-C_0$	+5.11	+11.82	+22.11
$I_a+I_c-I_b-(I_a+I_c-I_b)_0$ (amu·Å^2)	+0.16	+0.56	−0.03
Energy level (cm^{-1})	155±15	300±15	380±15
	$\overline{\mathrm{CD_2CH_2CD_2CD}}{}^{35}\mathrm{Cl}$		
$A-A_0$	−51	−97	
$B-B_0$	+3.75	+8.24	
$C-C_0$	+3.46	+7.85	
$I_a+I_c-I_b-(I_a+I_c-I_b)_0$ (amu·Å^2)	+0.36	+0.65	
Energy level (cm^{-1})	110±20	220±20	
	$\overline{\mathrm{CH_2CD_2CD_2CD}}{}^{35}\mathrm{Cl}$		
$A-A_0$	−53	−99	
$B-B_0$	+3.51	+7.56	
$C-C_0$	+3.91	+8.55	
$I_a+I_c-I_b-(I_a+I_c-I_b)_0$ (amu·Å^2)	+0.24	+0.40	
Energy level (cm^{-1})	120±20	240±40	

tion centered about 280 cm^{-1} were observed.[19] The 371-cm^{-1} absorption was assigned to the A' species of the carbon–chlorine bending mode, ν_β.

From the variation of the moments of inertia and of the energies, the lowest two levels were assigned to the excited ring puckering mode ν_α, and the level at ~380 cm^{-1} was assigned to the C–Cl bending mode. Additional evidence for this assignment was given by the values of $\sum m_i b_i^2 = \frac{1}{2}(I_a+I_c-I_b)$ in Table XII. This sum which depends upon distances perpendicular to the C–Cl bending motion would be expected to change in a ring puckering vibration but be unchanged in a C–Cl bending motion. The state at ~380 cm^{-1} leaves this sum unchanged corresponding to the C–Cl bending. Also the infrared absorption observed at 371 cm^{-1} appears strong and exhibits a strong central Q branch, whereas the absorption at 280 cm^{-1} appears weak and broad with no definite Q branch. The 371-cm^{-1} transition appears to correspond to a $\Delta n=1$ transition while the 280-cm^{-1} transition is broad and weak and appears to be a $\Delta n=2$ transition.[20]

Strauss and Russell[21] have observed the spectrum of cyclobutyl chloride in their far-infrared grating spec-

---

[19] The 280-cm^{-1} absorption is so broad that the center of the line is quite uncertain.

[20] See p. 1328, of the second paper of Ref. 4. Actually both of these transitions would be hybrids of both || and ⊥ types. Since $\mu_a/\mu_c \cong 3$, the ratio of the || and ⊥ contribution to the intensities would be approximately 9:1 for the $\Delta n=1$ transitions and 1:9 for the $\Delta n=2$ transitions.

[21] Private communication.

trometer. The data was taken early in the development of their instrument and is not of the quality currently possible. The position of the $\nu_a=0\leftrightarrow\nu_a=1$ transition appeared as a sharp Q branch at 158.5 cm^{-1}. The higher members of the series were not seen except for a possible band at about 145 cm^{-1}. This is the region in which the $\nu_a=1\leftrightarrow\nu_a=2$ line should appear, but observation was not sufficiently certain to be regarded as evidence one way or the other.

The energy of separation of the first two ring puckering levels will then be taken as 158.5 cm^{-1} to correspond to the infrared observation (consistent with the microwave value of 155 ± 15 cm^{-1}). The second separation from microwave intensities is then 141 ± 15 cm^{-1}.

Several possibilities exist for the potential function and these are shown in Fig. 1. As the angle of ring puckering increases, the potential function would tend to become more steep than a parabola. This factor alone would tend to make the frequency of the $0\leftrightarrow1$ transition lower than that of the $1\leftrightarrow2$ transition. As the molecule is distorted toward the planar configuration, two possibilities exist. One is that the energy of the planar form and possible configuration with Cl axial is very high. Here the potential function would be at least nearly as steep as a parabola, and the energy level spacing would increase with energy, as the curves in Case *A*. Conversely, if the energy of the planar configuration and possible axial chlorine forms were relatively low, the energy separation would decrease with energy, as in Curves *B*. The data on the energy separation is not conclusive but it does favor the relatively low planar energy of Curves *B*.

Some additional evidence favoring Curves *B* may be found by observing the effective angle of ring bending as calculated from the moments of inertia for the three states of the ring puckering vibration. These are 20° for the ground state, 17° for the first excited state, and 14° for the second excited state.[22] If the vibration were nearly symmetrical about the equilibrium configuration, as in Case *A*, there would be a much smaller or probably a slightly opposite trend.

In cyclobutyl fluoride a similar type of potential function is indicated. Here the microwave intensity measurements indicate the energy levels are more or less equally spaced with 140 ± 20 cm^{-1} between levels.

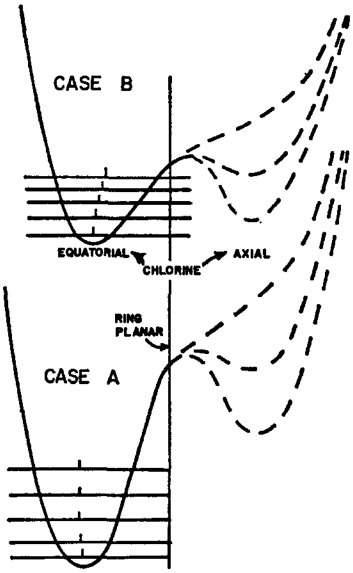

FIG. 1. Possible potential functions for cyclobutyl chloride. Case *A* has a high planar energy and a vibrational spacing which increases with energy. Case *A* is less probable than Case *B* which has a low planar energy. In Case *B* the energy level spacing and the effective angle of bending both decrease with increasing energy. Configurations with the chlorine in an axial position were not observed so that the shape of the curve in that region is indefinite.

The effective angles of ring puckering are 20°, 15.8°, 12.3°, and 8.6° for the first four levels. A potential function of this type for Case *B* is again indicated.

In Fig. 1, there are several curves shown for the potential function with the halogen in an axial position. Such a form might be unstable as shown in Curve B_1, or it might be stable as in B_2 or B_3. In this work, the only spectra observed were the forms with halogen in the equatorial configuration. A thorough search in the spectral region of 8 to 30 Gc/sec failed to detect any spectral lines that could be attributed to the presence of the axial form. If the halogen in an axial position corresponds to a stable configuration it must be at an energy of at least 400 cm^{-1} above the ground-state configuration which has the halogen in the equatorial configuration.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation and the California Research Corporation for financial support and to the University of California Computer Center at Berkeley. We wish to thank H. Strauss and J. Russell for helpful discussions and for the use of their unpublished infrared data.

---

[22] In calculating these effective ring angles, we have varied the two dihedral angles θ and ϕ relative to the ground-state structure. $\Delta\theta$ is obtained when the ring bends while holding the C_β–C_β distance constant, and $\Delta\phi$ when the ring bends while holding the C_α–C_γ distance constant. All other structural parameters were assumed to be the same as in the ground state. The angles quoted are the values of the angle θ in the various excited states.